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The Effect of Different Biochar on the Mechanical Properties of Cement-Pastes and Mortars

Daniel Suarez-Riera [1,*], Devid Falliano [1], Juan Felipe Carvajal [1], Adriana Carolina Bravo Celi [1], Giuseppe Andrea Ferro [1], Jean Marc Tulliani [2], Luca Lavagna [2,*] and Luciana Restuccia [1]

[1] Department of Structural, Geotechnical and Building Engineering, Politecnico di Torino, Corso Duca Degli Abruzzi, 24, 10129 Turin, Italy; devid.falliano@polito.it (D.F.); juan.carvajal@studenti.polito.it (J.F.C.); adriana.bravoceli@polito.it (A.C.B.C.); giuseppe.ferro@polito.it (G.A.F.); luciana.restuccia@polito.it (L.R.)

[2] Department of Applied Science and Technology, Politecnico di Torino, Corso Duca Degli Abruzzi, 24, 10129 Turin, Italy; jeanmarc.tulliani@polito.it

* Correspondence: daniel.suarez@polito.it (D.S.-R.); luca.lavagna@polito.it (L.L.); Tel.: +39-011-090-4598 (D.S.-R. & L.L.)

Abstract: In recent years, there has been a concerning surge in CO_2 emissions, with the construction and materials production sectors standing out as significant contributors to greenhouse gas pollution. To tackle this pressing environmental challenge, architectural design and civil engineering are actively pursuing strategies to mitigate their carbon footprint. These initiatives include adopting eco-friendly construction materials with reduced toxicity, rigorous energy management practices across the entire life cycle of structures, and incorporating innovative materials like biochar. Biochar is a carbon-rich byproduct generated through controlled thermochemical processes, such as pyrolysis or gasification, that stands out for its remarkable capacity to extract energy from processed biomass while delivering substantial environmental advantages. This study examines the use of biochar as a filler in cement-paste and mortar, as well as its influence on mechanical properties. In the case of cementitious pastes, results show that small amounts of biochar (1-2-5% by weight of cement) can improve the compressive and flexural strength, as well as fracture energy, thus generating a more tortuous crack path that increases the final surface area. In mortar specimens, the biochar influence does not show similar patterns or characteristics as the cement-paste in flexural and compressive strengths; nevertheless, biochar particles improve the toughness.

Keywords: cement-paste; mortar; waste valorization; mechanical properties; biochar

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1. Introduction

As the United Nations (UN) recently reported, the world's population has reached 8 billion inhabitants, and will continue to grow to around 10.4 billion by the 2080s [1]. The main repercussion of demographic growth is an increment in waste production, as well as CO_2 emissions [2]. For instance, annual global CO_2 emissions have reached nearly 32 billion tons, which is over 50% more than the emissions from three decades ago, contributing to climate change and ecological damage [3]. The Global Alliance for Buildings and Construction estimates that the construction industry is responsible for about two-fifths of all energy-related CO_2 emissions [4]. Furthermore, over one-third of CO_2 emissions from construction operations, and nearly 8% of all anthropogenic CO_2 emissions, have been caused by cement manufacture, the most widespread building material globally [5]. Therefore, much work will be needed to develop and promote carbon-negative building materials through cutting-edge design, as well as unprecedented measures, if global carbon neutrality targets are to be met.

A critical environmental challenge is the failure to recycle nearly half of the waste produced by the United States, Germany, the United Kingdom, and Australia. This is equivalent to over 82 million tons annually [6].

Nearly one-third of the foods produced for human intake (1.3 billion tons per year), are wasted [7]. Approximately 50 million cubic meters of wood waste are generated each year in the European Union [8]. Finally, a significant fraction of the post-consumer textile waste is not recycled, but instead is either disposed of in landfills, or thermochemically treated for energy production [9]. The European Union (EU) recently introduced legislation to promote the recycling and reusing of materials to address the waste problem. The industrial sector, particularly the wood sector, is intervening in waste reduction by managing wood waste, and avoiding the environmental threat caused by its constant accumulation [10,11]. Consequently, wood waste can be transformed into valuable products to encourage a more sustainable and unpolluted environment by recovering energy through using thermochemical processes like gasification or pyrolysis [12]. These processes transform biomass into liquid biofuel or syngas, and produce biochar, a secondary product that has drawn interest because it can store carbon and enhance soil quality [13–15]. Similarly, the building sector has begun to contemplate its application.

Biochar is an enriched carbon biomaterial developed via slow pyrolysis; it consists of biomass combustion in a low-oxygen environment [16,17]. The biomass required to produce biochar can come from agricultural or municipal waste decomposition, and molecular cracking at temperatures between 300 and 1000 °C [14]. Furthermore, biochar can store more than three-fifths of its original carbon mass, depending on the preparation inputs employed. Each metric ton of dry feedstock can cut 530–570 kg of carbon dioxide from net greenhouse gas emissions [18]. Thus, cement-based building materials can become more sustainable through adding charcoal filler to the mix, resulting in a considerable environmental improvement for the construction industry. The main criteria for considering biochar suitable for construction are its low thermal conductivity, reduced flammability, and high chemical stability [19]. Moreover, the pyrolysis process defines the pore distribution in biochar, which lowers the thermal conductivity, and contributes to reducing energy consumption in buildings [20]. Regarding flammability, Zhao et al. propound that slow pyrolysis procedures generate non-flammable biochar, while fast pyrolysis biochar has a higher presence of combustible compounds [21]. Likewise, Restuccia and Ferro demonstrated that pyrolyzed coffee powder and hazelnut shells biochar present different results depending on their characteristics; therefore, it is crucial to understand the outcomes produced by various raw materials and manufacturing processes [22].

Some studies indicate that adding biochar to cement-based materials can improve their mechanical properties [22–24]. Reviewing the application of biochar in cement-paste illustrates some promising results. For example, Suarez-Riera et al. [25] observed that adding 1% and 2% of biochar composites improved the flexural strength of cement-paste by up to 24% and 15%, respectively. Restuccia and Ferro [26] evaluated the use of food waste, particularly hazelnut shell biochar, as a cement-paste micro-aggregate. The results demonstrated that a 0.8–1% biochar addition substantially improved compressive and flexural strength, fracture toughness, and ductility. Specifically, the fracture energy showed an increment of up to 130%, and the modulus of rupture a 22.2%. In addition, these authors demonstrated that pyrolyzed coffee powder biochar improved compressive and flexural strength, as well as fracture energy, which is contrary to the standard behavior of cement-paste in which an increase in strength makes the material more brittle [19].The use of these materials, however, involves an increase in the costs of production of the final cementitious material, as they have high production costs. In using biochar, on the other hand, production costs are reduced since biochar derives from waste materials [27].

On the other hand, replacing a percentage of cement in mortars with biochar demonstrates performant outcomes. Choi et al. [28] proved that by substituting up to 5% of cement with wood waste biochar, the compressive strength of mortar rose by 10–12%. The internal curing properties benefited from the water released from the biochar pores, causing compressive strength to rise. These benefits in hydration occur in both wet and dry exterior curing conditions. Suarez-Riera et al. demonstrated that using 2% of biochar as a filler in mortar specimens resulted in improvements to fracture energy of approximately 40% com-

pared to the reference mix [27]. Gupta et al. [23,29,30] claim that the free water-cement ratio can be controlled by incorporating 1–2% biochar and, therefore, the mechanical strength, flexibility, and durability of cement mortar and concrete can increase by up to 20% and 50%, respectively.

The available research proves that biochar successfully improves the performance of cementitious materials, specifically cement-paste and mortars. Regardless of the many benefits associated with including biochar in cement-based mixes, an optimal mix design is yet to be identified since varied outcomes have been observed from different manufacturing processes and raw materials of the biochar utilized. In addition, the effect of adding biochar differs depending on the properties of the biochar itself, and on the type of cementitious system to which it is added. Due to its porosity and chemical structure, biochar tends to reduce the workability of the mixture, a problem that is still present and poorly studied in the literature [31–33]. To highlight these two different influences, this investigation focuses on characterizing two biochar types derived from gasification and pyrolysis treatment waste, and examines their impact on the mechanical performance of cement-paste and mortar samples when 1%, 2%, and 5% (by weight of cement) of biochar is added as filler. The novelty of this study lies in the desire to study the behavior of the same biochar when added to pure cement-pastes, and when added to mortars obtained using the same type of cement. The analysis of the mechanical properties constitutes a flexural strength and fracture energy evaluation together with a compressive strength test, alongside the biochar's characterization results from a water absorption analysis. This is followed by the particle size distribution assessment, a Brunauer–Emmett–Teller (BET) analysis, a Field emission scanning electron microscopy (FE-SEM) image study, and a thermogravimetric analysis (TGA).

2. Materials and Methods

2.1. Materials

Portland cement (c) type I 52.5R (Buzzi Unicem S.r.l., Casale Monferrato, Italy), MasterEase superplasticizer (SP) (Master Builders Solutions Italia S.p.A., Treviso, Italy), and tap water (w) have been used to produce cement-paste; in the case of mortars, CEN Standard sand (Societé Nouvelle Du Littoral and according to UNI EN 196-1:2006 [34]) was also added. Furthermore, two different biochar were employed: Borgotaro (BB) and Nera Biochar (NB) provided by VIS Energy S.p.A. (Fontanelle, Italy) and Nera Biochar S.r.l. (Montestrutto, Italy), respectively (Figure 1).

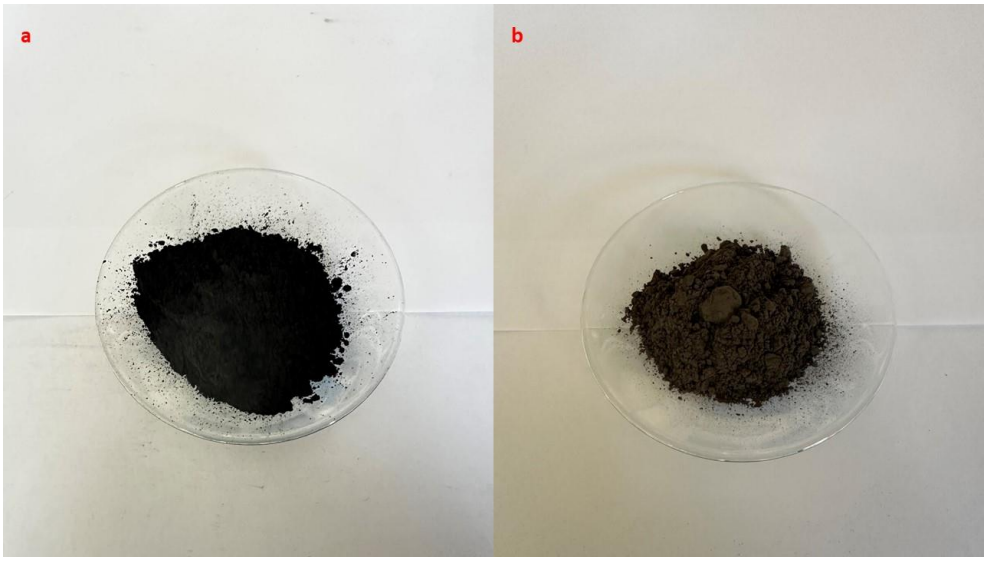

Figure 1. Appearance of Nera Biochar (**a**) and Bogotaro Biochar (**b**).

2.2. Biochar Characterization

The production of BB involved the gasification of wood chips at a temperature of approximately 700 °C. On the other hand, NB is a commercial product obtained from wood waste and manufactured in Turin, Italy. NB was initially designed for agricultural use, resulting in particle sizes ranging from 0.5 to 5 mm. In order to optimize its effectiveness as a filler in cement mixes, previous studies have suggested that reducing the average particle size of the biochar may be beneficial because in increasing the surface area of the biochar particles, greater interaction between the particle and the cement matrix will be obtained [24,29,35]. As a result, the NB was ground for 7 h using a ball milling machine.

Finally, both biochar powders underwent a water absorption test; additionally, laser granulometry was used to analyze the particle size using a Malvern Masterease 3000 Aeros S machine. The morphology of samples was observed through a HITACHI FESEM at 10 kV, and increased by more than 5 K. To determine the specific surface area and pore volume of Borgotaro and Nera biochar, the Brunauer-Emmett-Teller (BET) analysis method was used with a TriStar II Krypton 3020 V1.03 through N_2 physisorption analysis at a temperature of −77 K. Before analysis, the samples were degassed at 200 °C for 2 h to remove moisture/water adsorption and pollutants from the atmosphere. Lastly, the thermogravimetric analysis (TGA) was performed to understand whether a thermal treatment may deteriorate the material. A Mettler Toledo model 1600 was used for the TGA. The analysis was carried out through heating the sample (about 35 mg) at a rate of 10 °C/min up to 1000 °C in a flowing air atmosphere at a rate of 50 mL/min.

2.3. Samples Preparation

Four types of cement-paste and mortar samples were prepared, the reference samples and three batches with the addition of the different percentages of biochar by weight of cement, 1%, 2%, and 5%, used as filler. These percentages were chosen based on previous articles by some of the authors [22,25,36]. The biochar was added by first dispersing it in the water needed for cement-paste and mortar.

To prepare the cement-paste (C), the cement powder was slowly added to a water-superplasticizer-biochar solution, and stirred for five minutes. The cement paste, prepared at a water-to-cement (w/c) ratio of 0.35, and containing 1% by weight of cement of SP, was then poured into prismatic molds of size 20 × 20 × 80 mm. However, it is essential to highlight that the 5%-BBC study case was impossible to cast due to workability problems. On the other hand, all mortar mixtures (M) were prepared with a water-to-cement ratio of 0.50, a cement-to-aggregate ratio of 1:3, and mixed according to UNI EN 196-1:2006 [34]. Following the standard, a mixture of water and cement was stirred for 30 s to start the process. The sand was then gradually added within the first 30 s of mixing. After that, all the ingredients were mixed vigorously for the next 30 s. The mixer was then stopped for 90 s, during which time any remaining material on the bowl walls was cleared away in the first 30 s, and the mixture was allowed to rest for the remainder of the time. After the break, the mixer was started again at high speed for another 60 s. Once the mixing phase was complete, the mix was slowly poured into a steel mold consisting of three 40 × 40 × 160 mm prismatic specimens, taking care not to introduce air bubbles. All the materials were weighted according to the mix design in Table 1.

The cement-paste and mortar specimens were then placed in a humid environment at room temperature (24 ± 1 °C) with a relative humidity of at least 90% for 24 h. After demolding, the specimens were submerged in a water tank at 20 ± 1 °C, and allowed to mature for mechanical testing after 28 days.

Table 1. Mix design of cement-paste and mortar specimens.

Mix ID	Description	Cement [g]	Water [g]	SP [%] *	Sand [g]	Biochar [g]
0% C	Plain Cement-paste	460	161	1	-	0
1%-BBC	Cement-paste with 1% of Borgotaro biochar as filler	460	161	1	-	4.6
1%-NBC	Cement-paste with 1% of Nera biochar as filler	460	161	1	-	4.6
2%-BBC	Cement-paste with 2% of Borgotaro biochar as filler	460	161	1	-	9.2
2%-NBC	Cement-paste with 2% of Nera biochar as filler	460	161	1	-	9.2
5%-BBC	Cement-paste with 5% of Borgotaro biochar as filler	460	161	1	-	23
5%-NBC	Cement-paste with 5% of Nera biochar as filler	460	161	1	-	23
0% M	Plain Mortar	450	225	-	1350	0
1%-BBM	Mortar with 1% of Borgotaro biochar as filler	450	225	-	1350	4.5
1%-NBM	Mortar with 1% of Nera biochar as filler	450	225	-	1350	4.5
2%-BBM	Mortar with 2% of Borgotaro biochar as filler	450	225	-	1350	9.18
2%-NBM	Mortar with 2% of Nera biochar as filler	450	225	-	1350	9.18
5%-BBM	Mortar with 5% of Borgotaro biochar as filler	450	225	-	1350	22.5
5%-NBM	Mortar with 5% of Nera biochar as filler	450	225	-	1350	22.5

* by weight of cement.

2.4. Mechanical Tests

To evaluate the influence of biochar powder used as filler in cement-paste and mortar samples, a three-point bending test (TPB) in crack mouth open displacement (CMOD) (Figure 2) and a compressive test (Figure 3) were performed to evaluate the flexural strength, fracture energy, and compressive strength. Before performing the TBP test, a u-notch of 6 mm and 12 mm depth for cement-paste and mortar samples, respectively, and 2 mm width was made in each sample using a Miter saw BRILLANT 220. The notch was made in the middle of the orthogonal face to the specimens' pouring surface. Each result of compressive and flexural strength averaged at least four measurements.

Figure 2. Three-point bending test in crack mouth open displacement.

Figure 3. Compressive test.

Flexural analysis was performed following the Japan Concrete Institute Standard JCI-S-001 [37], with a single-column Zwick-Line Z050 with a cell load of 1 kN for cement-paste samples, and 50 kN for mortar samples, with a pre-load of 5 N, a span of 70 mm and 12 mm for cement-paste and mortar specimen, respectively, and a test speed of 0.005 mm/min. The flexural strength was calculated through:

$$\sigma_f = F_{max} \cdot \frac{3L}{2bh^2} \quad [\text{MPa}] \tag{1}$$

where F_{max} is the force on the prism at the failure time, L is the span, b is the specimen depth, and h is the net ligament height.

In quasi-brittle materials, the Japan Concrete Institute Standard JCI-S-001 [37] describes the process of finding the TPB test's fracture energy, measuring the amount of energy absorbed until the samples break into two prisms. After the TPB test, the following calculation was performed:

$$G_F = \frac{0.75W_0 + W_1}{A_{lig}} = G_{F0} + G_{Fcorr} \quad [\text{N/mm}^2] \tag{2}$$

where A_{lig} is the area of the nominal ligament, W_0 [N·mm] is the area below the CMOD curve up to the rupture of the specimen, and W_1 [N·mm] is the work done by deadweight of specimen and loading, evaluated as:

$$W_1 = 0.75\left(\frac{l}{L}m_1 + 2m_2\right)g \cdot CMOD_c \quad [\text{N·mm}] \tag{3}$$

where l is the loading span, L is the total length of the specimen, m_1 [kg] is the mass of the notched specimen, m_2 [kg] is the mass composed via the arrangement for the evaluation of the displacement placed on the beam until it breaks, without being attached to the testing machine, g is the gravity acceleration, and $CMODc$ is the crack mouth opening displacement at the rupture.

The two halves obtained through TPB were used to evaluate the compressive strength. Compressive tests were performed following the UNI EN 196-1:2005 [36], using the same machine with a load cell of 50 kN, a pre-load of 30 N, and a test speed of 600 N/s for cement-paste samples. Regarding the mortar's compressive test, a single-column Zwick-Baldwin testing machine with a load cell of 500 kN, and a test rate velocity equal to 2400 N/s was employed. The compressive strength was evaluated as follows:

$$\sigma_{c,max} = \frac{F_{max}}{bh} \quad [\text{MPa}] \tag{4}$$

where F_{max} is the maximum force supported by the specimen before rupture, and b and h are the specimen thickness to 40 mm by side.

3. Results

3.1. Biochar Characterization

3.1.1. Water Absorption

According to Gupta et al. [29], water retention by biochar makes it a potential material in cementitious matrix thanks to their morphology and surface pores; furthermore, Gray et al. [38] reported that micro-pores and pyrogenic nano-pores provide a site for the adsorption of aqueous solutions.

The water retention capacity of the biochar was determined using the method used by Gupta et al. [29]. Firstly, 30 g of biochar was dried in a continuous airflow oven at 70.3 °C for 24 h to eliminate any moisture present in the powder. Next, three containers were prepared, each containing 10 g of biochar, and 100 g of previously weighed deionized water. The containers were sealed and left to stand for 48 h. Afterward, each solution was filtered using a cellulose filter under vacuum until there was no free water flow. The weight of the soaked biochar was then subtracted from the weight of the dry biochar, and the mass of water absorbed in the biochar was calculated. The water retention capacity was expressed as the mass of absorbed water per gram of dry biochar, and was calculated to be 2.17 g and 0.97 g of water per gram of dry biochar for BB and NB, respectively. The results show that NB has a significantly lower water retention capacity than BB.

3.1.2. Particle Size Distribution

The particle size distribution for BB, NB, and cement powder are shown in Figure 4. The distribution shows that approximately 80% of the Biochar particles are below 20 µm, and the average particle size (D × 50) for BB and NB is 8.2 µm and 7.9 µm, respectively. In addition, approximately 10% of the biochar particles have a size below 1.5 µm in both cases.

3.1.3. Brunauer-Emmett-Teller Analysis (BET)

The results for BB showed a specific area of almost 30 m^2/g and a pore size of 3.3 nm. On the other hand, the analysis for NB showed a specific area of 25.3 m^2/g and an average pore size of 1.2 nm, as calculated through the BET [39]. These conditions facilitate the access to the adsorption of water [38]. There is a correlation between pore size and water absorption since BB has shown a two times higher water adsorption than NB. A summary of the biochar characterization is shown in Table 2.

Table 2. Biochar characterization.

Biochar	Water Absorption [g/gdbc] *	Particle Size (D × 50) [µm]	Surface Area [m^2/g]	Average Pore Size [nm]
Borgotaro	2.17	8.2	30	3.27
Nera	0.97	7.9	25.27	1.22

* g/gdbc = gram of water per gram of dry biochar.

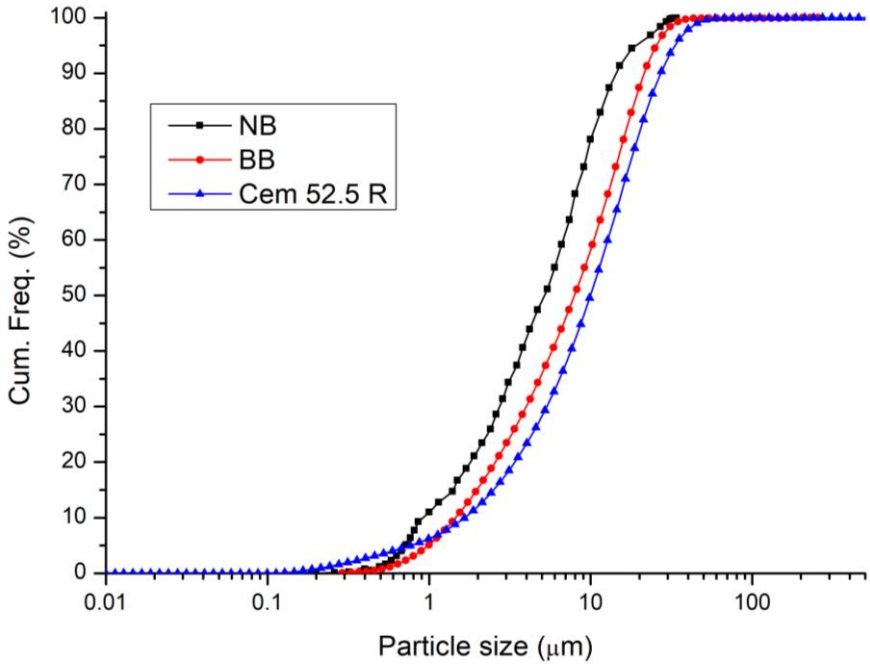

Figure 4. Particle size distribution of Borgatoro, Nera biochar and cement powder.

3.1.4. FESEM

FESEM images of the two different biochar used in this research are shown in Figure 5. It can be observed that the biochar maintains part of the biomass fibrous structure, and is clearly seen to be porous in all the images. The porous structure of biochar derives from the porous structure existing in raw biomass, but can also be due to the production process. The surface of Borgotaro biochar showed a high porosity (Figure 5c), in accordance with what has already been shown in the previously reported characterization tests.

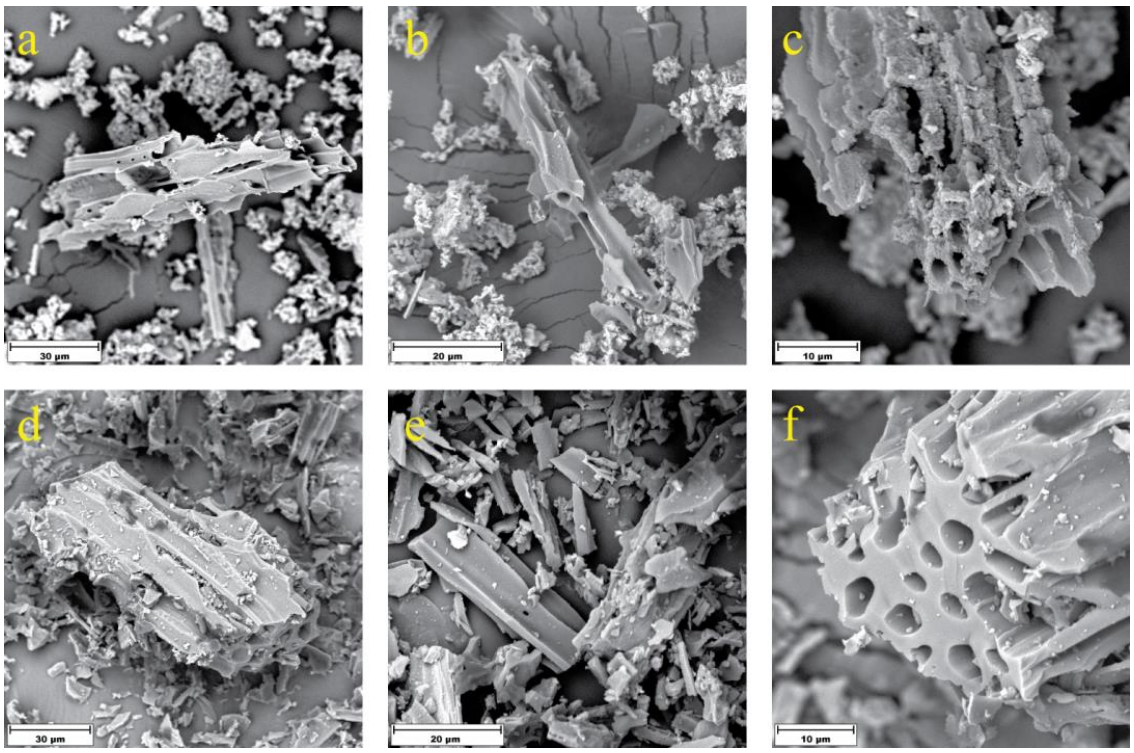

Figure 5. FESEM images of Borgotaro biochar (**a**–**c**) and Nera biochar (**d**–**f**) from wood waste.

3.1.5. Thermogravimetric Analysis (TGA)

TGA curves are shown in Figure 6. The results reveal two main thermal phenomena; first, a weight loss (more than 5%) from 50 to 150 °C due to the desorption of water adsorbed in the biochar pores for both BB and NB samples, which is in accordance with Zhou et al. [40], followed by a significant weight loss that starts above 270 °C and continues until ca. 400 °C and 490 °C for BB and NB specimens, respectively, which is attributable to the decomposition of the carbonaceous residue from the production process, leaving a final residue at 1000 °C of ca. 5 wt% in both cases that can be attributed to the presence of inorganic compounds or metals. The BB has a slight lower thermal stability compared to NB. However, BB and NB are rather thermally stable due to the limited percent weight loss at the temperature ≤250 °C; a similar trend was reported by Kaikiti et al. [41].

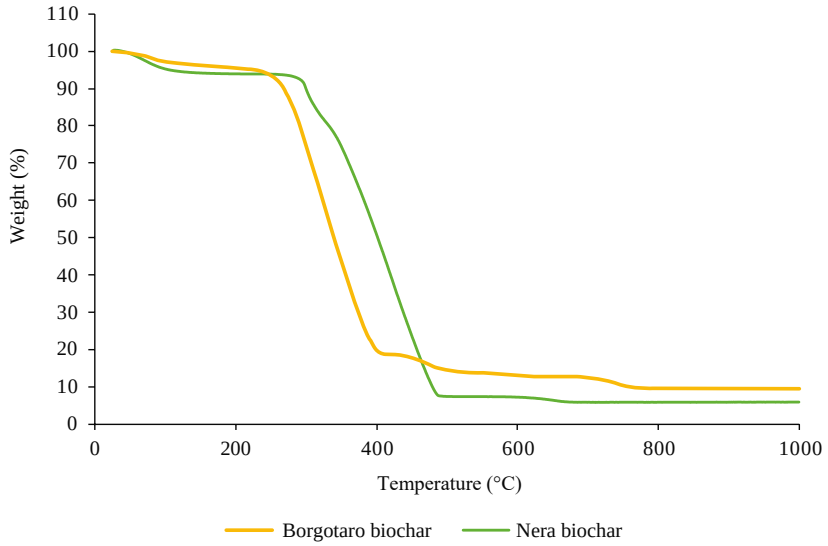

Figure 6. Thermogravimetric analysis (TGA) of Borgotaro and Nera biochar.

3.2. Mechanical Test Results

The flexural strength, fracture energy, and compressive strength results of cement-paste and mortar specimens are shown in Figure 7. The study case 5%-BBC's results are not displayed since the batch was impossible to cast; this condition can be caused due to the high water-absorption rate of the BB, which is more than two times higher than the NB, significantly affecting the workability of the mix.

Figure 7a,b represent, respectively, the results in terms of flexural strength (σ_f) and fracture energy (G_f) of the cement-paste and mortar specimens with biochar used as a filler at 28-days. On the one hand, the cement-paste sample results show how using 1% of BB and NB improved by almost 30% compared to pure cement, regardless of the biochar used. Furthermore, it is possible to observe a similar trend in the 2% BBC and NBC cases, which presented an improvement of approximately 20% compared to the reference (0% C). The 5% biochar analysis, only possible for NB, shows a slight decay in flexural strength compared with the lower substitutions; however, it is still moderately above the reference mix. On the other hand, for mortar specimens, the lowest biochar percentual substitution, namely 1%, provides an improvement of about 10% for both biochar used. These results contrast the finding reported by Tan et al. [42], in which adding 5% of pyrolyzed biochar at 500 °C caused a drop in flexural strength by around 20% at 28-days.

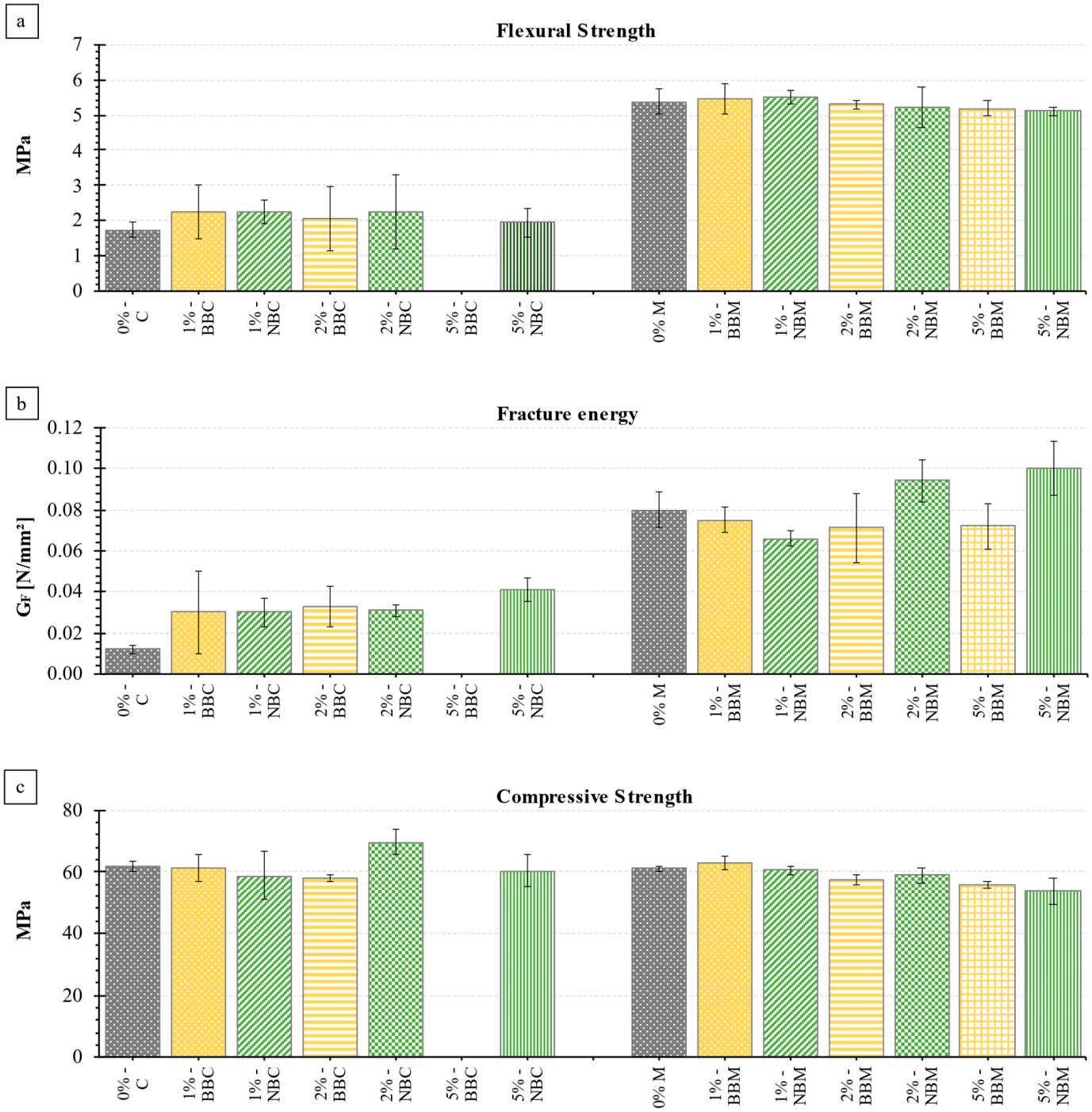

Figure 7. Flexural strength (**a**), Fracture energy (**b**) and Compressive strength (**c**) average value for each batch at 28 days.

Moving to fracture energy, results revealed an advantageous effect of biochar addition for both Borgotaro and Nera microparticles when used in cement-paste. Using 1, 2 and 5 wt% as filler of biochar led to an increase of more than 150, 175 and 240%, respectively, compared to the reference. According to Figure 7b, the fracture energy performance of the mortar specimens slightly decreased when BB was used. Specifically, using 1, 2, and 5% of BB resulted in reductions of more than 6%, 11%, and 10%, respectively, compared to the mortar without biochar. However, batches with 2% and 5% of Nera biochar showed improvements of more than 17% and almost 30%, respectively, concerning the reference. Based on these results, the beneficial effects on fracture energy highlighted in the case

of cement-pastes are not always present, and undoubtedly less significant, in the case of mortars, although they are still evident, and by no means negligible, for the NB in the percentages of 2% and 5%.

The compressive strength (σ_c) results at 28-days of cement-paste and mortar specimens incorporating various dosages of biochar are displayed in Figure 7c. The results obtained from testing cement-paste specimens showed favorable outcomes when using NBC. The compressive strength of the 2% NBC batch slightly improved by almost 15% compared with the reference sample. Furthermore, using a percentage of NB equal to 5% gave a positive result; in this case, the compressive strength remained approximately the same compared to plain cement-paste. Concerning cement-pastes, adding biochar does not trigger significant decreases in compressive strength. Regarding mortars, adding biochar does not generate significant changes in compressive performance; conversely, it decreases as the dosage of both biochar used in this study increases.

4. Discussion

The flexural test results for cement paste show an overall improvement in strength with low biochar content. This improvement in mechanical properties is associated with the "bridging effect", which is particularly evident in fracture energy, where both types of biochar tend to enhance performance compared to standard cement. Furthermore, as indicated in the literature [43], biochar can serve as a nucleation point for the hydration phases of cement, promoting better maturation.

At higher biochar contents, the negative mechanical effect is primarily due to the high surface area and numerous pores that tend to sequester hydration water, as shown in Table 2. This phenomenon worsens the workability of the composite and further lowers the water-to-cement ratio, thereby not ensuring sufficient water for optimal cement hydration and deteriorating performance [44]. This effect has also been observed in the literature by Tan et al. [42], although the flexural strength decrease is less pronounced in our case.

In the case of mortar, there is a slight improvement in mechanical performance in both flexural and compressive strength, with fracture energy improving only when using NB. The bridging effect is less apparent in this case, while the impact related to biochar size is more pronounced. Given the sub-micrometric size of the biochar, as shown in Figure 4, it tends to fill the intrinsic microporosities of the mortar, leading to better packing of the cementitious system. In particular, NB has smaller particle sizes than BB, resulting in higher resistance to crack propagation and strength development [45]. However, at higher biochar contents, both types tend to worsen flexural and compressive strength, an effect attributed to poor biochar dispersion within the matrix, leading to imperfect filler distribution [29].

The performance of fracture energy aligns with other findings in the literature. Biochar can enhance the tortuosity of the failure path in cement paste samples, altering the crack path trajectory, especially due to the fine particles it contains [46]. Therefore, adding fine biochar particles results in improved packing and a more densely packed matrix, effectively transferring stress through the composite [47].

The results obtained for compressive strength contradict those in the literature. Chen et al. [48] found that adding 3% of biochar improved compressive strength by almost 20% after 28 days. Additionally, Liu et al. [49] reported a 29.3% improvement when 2% of bamboo biochar was used in mortars. Nevertheless, the compressive strength results in this study conform to American and European standards governing the strength and capacity of mortar samples [50]. As with flexural strength and fracture energy, the most significant effects of adding biochar can be observed in cement pastes. It is worth noting that adding biochar up to 2% does not lead to significant reductions in mortar compressive strength.

5. Conclusions

This study investigated the potential benefits of using two types of biochar, Borgotaro (BB) and Nera (NB), as a filler in cementitious composites (cement-paste and mortar) to

enhance their mechanical properties, and reduce their carbon footprint. Both biochar types were produced using a standardized gasification process and pyrolysis of wood waste.

The results indicated that adding BB and NB increased flexural strength in all cases for the cement-pastes, giving them a more tough behavior, as shown by the significant increase in the fracture energy obtained through adding biochar to the cement-pastes. For example, with a 2% biochar substitution, both types of biochar increased the flexural strength by 20% compared to the reference sample, and increased fracture energy by 150%. On the other hand, NB, characterized by smaller particle size and lower internal porosity than BB, allows for not negligible increases in compressive strength equal to just under 15% when adding 2% biochar to cement-pastes. On the other hand, there are no appreciable variations in the compressive strength in the other cases. The beneficial effects obtained in the case of cement-pastes are dampened in the case of mortars while remaining appreciable as the fracture energy for NB is increased by 2%. However, for mortars, the flexural strength and the compressive strength for percentages of biochar equal to 2% remain virtually identical to the reference sample, which is undeniably positive and applicable in the practical field. In fact, it is possible to exploit biochar as a secondary material to obtain mortars with a lower environmental impact characterized by higher fracture energy without any deterioration in the mechanical resistance.

The improvements of mechanical properties are due to biochar that acts as a micro-reinforcement in the cementitious paste, contributing to a more compact matrix, and an increase in the toughness of a brittle material. In the case of mortars, fine aggregate substantially reduces these beneficial effects, which remain non-negligible for the post-peak behavior of samples subjected to three-point bending tests.

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References

1. United Nations. Department of Economic and Social Affairs, Revision of World Population Prospects. 2022. Available online: https://population.un.org/wpp/ (accessed on 18 November 2022).
2. Nwakaire, C.M.; Yap, S.P.; Onn, C.C.; Yuen, C.W.; Ibrahim, H.A. Utilisation of recycled concrete aggregates for sustainable highway pavement applications; a review. *Constr. Build. Mater.* **2019**, *235*, 117444. [CrossRef]
3. International Energy Agency (IEA). *Global Energy Review: CO_2 Emissions in 2021*; IEA: Paris, France, 2021.
4. Nasir, M.H.A.; Genovese, A.; Acquaye, A.A.; Koh, S.; Yamoah, F. Comparing linear and circular supply chains: A case study from the construction industry. *Int. J. Prod. Econ.* **2017**, *183*, 443–457. [CrossRef]
5. GHabert, G.; Miller, S.A.; John, V.M.; Provis, J.L.; Favier, A.; Horvath, A.; Scrivener, K.L. Environmental impacts and decarbonization strategies in the cement and concrete industries. *Nat. Rev. Earth Environ.* **2020**, *1*, 559–573. [CrossRef]
6. OECD. *Global Material Resources Outlook to 2060*; OECD: Paris, France, 2019. [CrossRef]
7. Gustavsson, J.; Cederberg, C.; Sonesson, U. *Global Food Losses and Food Waste: Extent, Causes and Prevention; Study Conducted for the International Congress Save Food! At Interpack 2011, [16–17 May], Düsseldorf, Germany*; Food and Agriculture Organization of the United Nations: Rome, Italy, 2011.
8. Bergeron, F.C. Energy and climate impact assessment of waste wood recovery in Switzerland. *Biomass-Bioenergy* **2016**, *94*, 245–257. [CrossRef]
9. Lopatina, A.; Anugwom, I.; Blot, H.; Conde, S.; Mänttäri, M.; Kallioinen, M. Re-use of waste cotton textile as an ultrafiltration membrane. *J. Environ. Chem. Eng.* **2021**, *9*, 105705. [CrossRef]

10. Adegoke, K.A.; Adesina, O.O.; Okon-Akan, O.A.; Adegoke, O.R.; Olabintan, A.B.; Ajala, O.A.; Olagoke, H.; Maxakato, N.W.; Bello, O.S. Sawdust-biomass based materials for sequestration of organic and inorganic pollutants and potential for engineering applications. *Curr. Res. Green Sustain. Chem.* **2022**, *5*, 100274. [CrossRef]
11. Alabduljabbar, H.; Huseien, G.F.; Sam, A.R.M.; Alyouef, R.; Algaifi, H.A.; Alaskar, A. Engineering Properties of Waste Sawdust-Based Lightweight Alkali-Activated Concrete: Experimental Assessment and Numerical Prediction. *Materials* **2020**, *13*, 5490. [CrossRef]
12. Basu, P. *Biomass Gasification, Pyrolysis and Torrefaction*; Elsevier: Amsterdam, The Netherlands, 2013. [CrossRef]
13. Cha, J.S.; Park, S.H.; Jung, S.-C.; Ryu, C.; Jeon, J.-K.; Shin, M.-C.; Park, Y.-K. Production and utilization of biochar: A review. *J. Ind. Eng. Chem.* **2016**, *40*, 1–15. [CrossRef]
14. Wang, J.; Wang, S. Preparation, modification and environmental application of biochar: A review. *J. Clean. Prod.* **2019**, *227*, 1002–1022. [CrossRef]
15. Agegnehu, G.; Srivastava, A.; Bird, M.I. The role of biochar and biochar-compost in improving soil quality and crop performance: A review. *Appl. Soil Ecol.* **2017**, *119*, 156–170. [CrossRef]
16. McGlashan, N.; Shah, N.; Caldecott, B.; Workman, M. High-level techno-economic assessment of negative emissions technologies. *Process. Saf. Environ. Prot.* **2012**, *90*, 501–510. [CrossRef]
17. Santos, F.M.; Gonçalves, A.L.; Pires, J.C.M. *Negative Emission Technologies, Bioenergy with Carbon Capture and Storage: Using Natural Resources for Sustainable Development*; Academic Press: Cambridge, MA, USA, 2019; pp. 1–13. [CrossRef]
18. Roberts, K.G.; Gloy, B.A.; Joseph, S.; Scott, N.R.; Lehmann, J. Life Cycle Assessment of Biochar Systems: Estimating the Energetic, Economic, and Climate Change Potential. *Environ. Sci. Technol.* **2010**, *44*, 827–833. [CrossRef]
19. Gupta, S.; Kua, H.W. Factors Determining the Potential of Biochar As a Carbon Capturing and Sequestering Construction Material: Critical Review. *J. Mater. Civ. Eng.* **2017**, *29*, 04017086. [CrossRef]
20. Brewer, C.E.; Brown, R.C. Biochar. In *Comprehensive Renewable Energy*; Elsevier: Amsterdam, The Netherlands, 2012; Volume 5, pp. 357–384. [CrossRef]
21. Zhao, M.Y.; Enders, A.; Lehmann, J. Short- and long-term flammability of biochars. *Biomass-Bioenergy* **2014**, *69*, 183–191. [CrossRef]
22. Restuccia, L.; Ferro, G.A. Promising low cost carbon-based materials to improve strength and toughness in cement composites. *Constr. Build. Mater.* **2016**, *126*, 1034–1043. [CrossRef]
23. Gupta, S.; Kua, H.W.; Koh, H.J. Application of biochar from food and wood waste as green admixture for cement mortar. *Sci. Total. Environ.* **2018**, *619–620*, 419–435. [CrossRef]
24. Maljaee, H.; Madadi, R.; Paiva, H.; Tarelho, L.; Ferreira, V.M. Incorporation of biochar in cementitious materials: A roadmap of biochar selection. *Constr. Build. Mater.* **2021**, *283*, 122757. [CrossRef]
25. Suarez-Riera, D.; Restuccia, L.; Ferro, G. The use of Biochar to reduce the carbon footprint of cement-based materials. *Procedia Struct. Integr.* **2020**, *26*, 199–210. [CrossRef]
26. Restuccia, L.; Ferro, G. Nanoparticles from Food Waste: A "Green" Future for Traditional Building Materials. In Proceedings of the 9th International Conference on Fracture Mechanics of Concrete and Concrete Structures, Berkeley, CA, USA, 29 May–1 June 2016.
27. Suarez-Riera, D.; Lavagna, L.; Bartoli, M.; Giorcelli, M.; Pavese, M.; Tagliaferro, A. The influence of biochar shape on cement-based materials. *Mag. Concr. Res.* **2022**, *74*, 1–6. [CrossRef]
28. Choi, W.C.; Yun, H.D.; Lee, J.Y. Mechanical Properties of Mortar Containing Bio-Char From Pyrolysis. *J. Korea Inst. Struct. Maint. Insp.* **2012**, *16*, 67–74. [CrossRef]
29. Gupta, S.; Kua, H.W.; Pang, S.D. Biochar-mortar composite: Manufacturing, evaluation of physical properties and economic viability. *Constr. Build. Mater.* **2018**, *167*, 874–889. [CrossRef]
30. Gupta, S.; Kua, H.W.; Low, C.Y. Use of biochar as carbon sequestering additive in cement mortar. *Cem. Concr. Compos.* **2018**, *87*, 110–129. [CrossRef]
31. Sikora, P.; Woliński, P.; Chougan, M.; Madraszewski, S.; Węgrzyński, W.; Papis, B.K.; Federowicz, K.; Ghaffar, S.H.; Stephan, D. A systematic experimental study on biochar-cementitious composites: Towards carbon sequestration. *Ind. Crop. Prod.* **2022**, *184*, 115103. [CrossRef]
32. Yang, X.; Wang, X.-Y. Hydration-strength-durability-workability of biochar-cement binary blends. *J. Build. Eng.* **2021**, *42*, 103064. [CrossRef]
33. Zhang, Y.; He, M.; Wang, L.; Yan, J.; Ma, B.; Zhu, X.; Ok, Y.S.; Mechtcherine, V.; Tsang, D.C.W. Biochar as construction materials for achieving carbon neutrality. *Biochar* **2022**, *4*, 59. [CrossRef]
34. *EN 196-1:2016*; Methods of Testing Cement—Part 1: Determination of Strength. Ente Nazionale Italiano di Unificazione: Roma, Italy, 2016.
35. Restuccia, L.; Ferro, G.A. Influence of filler size on the mechanical properties of cement-based composites. *Fatigue Fract. Eng. Mater. Struct.* **2018**, *41*, 797–805. [CrossRef]
36. Cosentino, I.; Restuccia, L.; Ferro, G.A.; Tulliani, J.-M. Influence of pyrolysis parameters on the efficiency of the biochar as nanoparticles into cement-based composites. *Procedia Struct. Integr.* **2018**, *13*, 2132–2136. [CrossRef]
37. Japanese Concrete Institute. *Method of Test for Fracture Energy of Concrete by Use of Notched Beam*; Japanese Concrete Institute: Tokyo, Japan, 2013; Volume 2, pp. 1–14.
38. Gray, M.; Johnson, M.G.; Dragila, M.I.; Kleber, M. Water uptake in biochars: The roles of porosity and hydrophobicity. *Biomass-Bioenergy* **2014**, *61*, 196–205. [CrossRef]

39. Brunauer, S.; Emmett, P.H.; Teller, E. Adsorption of Gases in Multimolecular Layers. *J. Am. Chem. Soc.* **1938**, *60*, 309–319. [CrossRef]
40. Zhou, H.; Ye, M.; Zhao, Y.; Baig, S.A.; Huang, N.; Ma, M. Sodium citrate and biochar synergistic improvement of nanoscale zero-valent iron composite for the removal of chromium (VI) in aqueous solutions. *J. Environ. Sci.* **2022**, *115*, 227–239. [CrossRef]
41. Kaikiti, K.; Stylianou, M.; Agapiou, A. Development of food-origin biochars for the adsorption of selected volatile organic compounds (VOCs) for environmental matrices. *Bioresour. Technol.* **2021**, *342*, 125881. [CrossRef]
42. Tan, K.; Pang, X.; Qin, Y.; Wang, J. Properties of cement mortar containing pulverized biochar pyrolyzed at different temperatures. *Constr. Build. Mater.* **2020**, *263*, 120616. [CrossRef]
43. Mensah, R.A.; Shanmugam, V.; Narayanan, S.; Razavi, N.; Ulfberg, A.; Blanksvärd, T.; Sayahi, F.; Simonsson, P.; Reinke, B.; Försth, M.; et al. Biochar-Added Cementitious Materials—A Review on Mechanical, Thermal, and Environmental Properties. *Sustainability* **2021**, *13*, 9336. [CrossRef]
44. Pantić, V.; Šupić, S.; Vučinić-Vasić, M.; Nemeš, T.; Malešev, M.; Lukić, I.; Radonjanin, V. Effects of Grinding Methods and Water-to-Binder Ratio on the Properties of Cement Mortars Blended with Biomass Ash and Ceramic Powder. *Materials* **2023**, *16*, 2443. [CrossRef]
45. Gupta, S.; Kua, H.W. Combination of Biochar and Silica Fume as Partial Cement Replacement in Mortar: Performance Evaluation Under Normal and Elevated Temperature. *Waste Biomass-Valoriz.* **2019**, *11*, 2807–2824. [CrossRef]
46. Restuccia, L.; Reggio, A.; Ferro, G.; Kamranirad, R. Fractal analysis of crack paths into innovative carbon-based cementitious composites. *Theor. Appl. Fract. Mech.* **2017**, *90*, 133–141. [CrossRef]
47. Moosberg-Bustnes, H.; Lagerblad, B.; Forssberg, E. The function of fillers in concrete. *Mater. Struct.* **2004**, *37*, 74–81. [CrossRef]
48. Chen, T.; Zhao, L.; Gao, X.; Li, L.; Qin, L. Modification of carbonation-cured cement mortar using biochar and its environmental evaluation. *Cem. Concr. Compos.* **2022**, *134*, 104764. [CrossRef]
49. Liu, W.; Li, K.; Xu, S. Utilizing bamboo biochar in cement mortar as a bio-modifier to improve the compressive strength and crack-resistance fracture ability. *Constr. Build. Mater.* **2022**, *327*, 126917. [CrossRef]
50. *EN 1992-1-1*; Eurocode 2: Design of Concrete Structures—Part 1-1: General Rules and Rules for Buildings. European Committee of Standardization: Brussels, Belgium, 2004.